



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C07C 2/12	A1	(11) International Publication Number: WO 94/12452 (43) International Publication Date: 9 June 1994 (09.06.94)
<p>(21) International Application Number: PCT/GB93/02407</p> <p>(22) International Filing Date: 23 November 1993 (23.11.93)</p> <p>(30) Priority Data: 9225183.4 2 December 1992 (02.12.92) GB</p> <p>(71) Applicant (for all designated States except US): THE BRITISH PETROLEUM COMPANY PLC [GB/GB]; Britannic House, 1 Finsbury Circus, London EC2M 7BA (GB).</p> <p>(72) Inventor; and (75) Inventor/Applicant (for US only): WADE, Steven, Ronald [GB/GB]; 50A Abbey Road, Chertsey, Surrey KT16 8NG (GB).</p> <p>(74) Agent: PREECE, Michael; BP International Limited, Chertsey Road, Sunbury-on-Thames, Middlesex TW16 7LN (GB).</p>		<p>(81) Designated States: AU, CA, JP, NZ, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Published <i>With international search report.</i></p>
<p>(54) Title: PROCESS FOR THE PRODUCTION OF BRANCHED OLEFINS</p> <p>(57) Abstract</p> <p>A process for the production of a product containing at least one C₄ and C₅ branched olefin comprising passing a feedstock containing ethene over a zeo-type catalyst in a reaction chamber wherein the feedstock also comprises at least one C₃-C₁₀ olefin and is present in the feedstock at a concentration of up to 50 % v/v relative to ethene and the zeo-type catalyst has a framework structure which includes a 10-member channel that is not intersected by another 10- or 12-membered channel.</p>		

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PROCESS FOR THE PRODUCTION OF BRANCHED OLEFINS

The present invention relates to a process for the production of a product rich in branched olefins by contacting an ethene feed with a minor proportion of higher olefins with a zeo-type catalyst.

5 Attempts to oligomerise ethene to provide low molecular weight hydrocarbon products have hitherto been relatively unsuccessful. Generally, products rich in aromatic hydrocarbons are obtained or polyolefins such as polyethylene often result.

Processes for the conversion of a C₂/C₃ mixed feed are
10 known. JP 0341036 relates to the conversion of an ethene/propene feed to yield C₅ olefins under relatively high pressure using an alkali metal based catalyst. The product is mainly 1-pentene. US
3 960 978 discloses the conversion of a C₂ to C₅ olefin feed over zeolite H-ZSM-5 to a range of liquid hydrocarbons. US 4 227 992
15 also discloses the conversion of a C₂ to C₆ olefinic feed over pentasil zeolite catalysts to produce liquid products. Under
chosen conditions, propene and butene conversions are 50-95%, but ethylene conversion is 10-20%.

We have now found that by introducing a minor proportion of
20 higher olefins into the ethene feed higher conversions of ethene can be achieved. The process provides a selective product rich in C₄ and C₅ olefins with low selectivity to less desirable aromatic products.

Accordingly, the present invention provides a process for the
25 production of a product containing at least one C₄ and C₅ branched

olefin which comprises passing a feedstock containing ethene over a zeo-type catalyst in a reaction chamber characterised in that the feedstock also comprises at least one C₃-C₁₀ olefin, and being present in the feed at a concentration of up to 50% v/v relative to ethene and the zeo-type catalyst having a framework structure which includes a 10-member channel that is not intersected by another 10- or 12- member channel.

The process of the present invention provides a product containing low molecular weight branched olefins with low selectivity to undesirable aromatic hydrocarbons.

The process of the present invention comprises passing an ethene feed containing at least one C₃ to C₁₀ olefin over a zeo-type catalyst under conditions capable of producing a product containing branched olefins. The olefinic feedstock comprises ethene and the C₃ to C₁₀ olefin wherein the C₃ to C₁₀ olefin is present at a concentration of up to 50% v/v, for example, from 1 to 50% v/v. Suitably, the C₃ to C₁₀ olefin is present from 1 to 40% v/v, especially from 10 to 35% v/v. The C₃ to C₁₀ olefin may suitably be a linear olefin or a branched olefin. Preferably the olefinic feedstock comprises ethene and at least one C₃ to C₅ olefin. Suitably, the C₃ to C₅ olefin is present in a concentration of up to 50% v/v. Advantageously, the C₃ to C₅ olefin accounts for the total C₃ to C₁₀ olefin feed. The preferred feed is a mixture of ethene and propene.

The olefin mixed feed of the process of the present invention may be derived from any suitable source. The feedstock need not be a high purity feed. Complex mixtures of olefins and streams containing alkanes, inert gas, hydrogen and carbon oxides may be used. Suitable sources of the olefins include those generated by refinery processes, e.g. fuel gas streams rich in ethene as typically described in "Oil and Gas Journal", page 94, April 20 1992. Mixed propene/propane and butene/butane streams produced as by-products of catalytic cracking are also particularly suitable for use as the C₃ to C₁₀ olefinic cofeed.

Light olefins including ethene are also produced in large

quantities by steam cracking of naphtha and higher hydrocarbons. Mixtures of olefins produced by the primary cracking process, impure streams generated as part of the separations process and mixtures of pure ethene and C₃ to C₁₀ olefin products are all
5 suitable feeds.

An ethene/C₃ to C₁₀ mixture may also be obtained through the conversion of oxygenates for examples alcohols, esters, ketones and aldehydes and higher hydrocarbon feeds. Typically, the conversion of methanol to predominantly ethylene and propylene can
10 be achieved with a zeolite SAPO catalyst as described in US 4374295 and EP-A-0418142. Additionally an ethene/C₃ to C₁₀ feed may also be derived via partial oxidation of suitable hydrocarbon feeds as disclosed in EP-A-0332289.

The zeo-type catalyst suitable for use in the process of the
15 present invention is one whose framework structure includes channels defined by 10-membered rings which are not intersected by channels having 10- or 12-membered rings. Zeo-type catalysts which may be used in the process include TON (Theta-1, Nu-10, ZSM-22, KZ-2, ISI-1), MTT (ZSM-23, EU-13, ISI-4, KZ-1), EUO (EU-1 TP2-
20 3, ZSM-50), AEL (SAPO-11) and FER (Ferrierite, FU-9, Nu-23, ISI-6, ZSM-35). These structures contrast with zeo-type catalysts with three dimensional channel structures such as MFI- and MEL-types which contain intersecting 10-ring channels and which tend to produce aromatics and saturated by-products. The preferred
25 zeo-type structures in the process of the present invention are TON and FER.

Information on zeo-type structures is given in the Atlas of Zeolite Structure types by Meier WM and Olsen DH, 1992 published by Butterworths, Zeolites vol 2, No 15, June 1992. All of the
30 above zeo-type structures can be prepared by published literature methods. Typical general methods are given, for example, in "Synthesis of High Silica Aluminosilicate Zeolites" by PA Jacobs and J A Martens, Studies in Surface Science and Catalysis, Vol 33, Elsevier, 1987, and "Zeolite Molecular Sieves" by D S Breck, John
35 Willey 1974.

A synthetic zeolite immediately after synthesis contains cations which, depending upon the precise synthesis method used, may be hydrogen, aluminium, alkali metals, organic nitrogen cations or any combination thereof. The zeo-type catalyst used in
5 the process of the present invention is preferably in the hydrogen form. The hydrogen form may be achieved by, in the case of organic containing zeo-type catalysts, calcination to remove the organics followed by either ammonium ion exchange or proton exchange with an acid solution or a combination of both. In the
10 case of a zeo-type catalyst synthesised in the absence of an organic nitrogen containing compound, the hydrogen form could be prepared by either direct ammonium ion-exchange followed by calcination or proton exchange with an acid solution or a combination of both. If so desired, the hydrogen form of the zeo-
15 type catalyst may suitably be partially exchanged or impregnated with a metal such as gallium or magnesium and used in the process of the present invention.

The zeo-type catalyst may be modified to alter its acidity or shape selectivity in such a way to improve the catalytic
20 performance. The modifications may include a calcination regime, steam treatment, acid/stream treatment, chemical treatment, e.g. with a dealuminating agent such as SiCl_4 , mineral acids, ammonium fluoride or bifluoride, EDTA etc or an aluminating agent such as sodium aluminate, aluminium chloride or inclusion of a phosphorus
25 compound, a Lewis base, hydrogen fluoride etc. The treatment step may be carried out during the preparation of the hydrogen-form or may be carried out after the preparation of the hydrogen form.

The zeo-type catalyst may be bound in a suitable binding material. Suitably, the binder may be one of the conventional
30 binders such as alumina, silica, clay or may be an aluminophosphate binder or a combination of binders.

The process of the present invention may be suitably carried out at a temperature of from 200 to 700°C, preferably 300 to 600°C. The process may be carried out under reduced or elevated
35 pressure relative to atmospheric pressure. Suitably a pressure of

from 0.1 to 100 bar absolute, preferably 0.5 to 50 bar absolute may be used.

The ethene and C₃-C₁₀ olefin streams may be passed into the reaction chamber separately and mixed therein. Alternately, the
5 two streams may be pre-mixed prior to passage into the reactor. Suitably, the gaseous streams may be pre-heated prior to contact with the catalyst. Suitably, the pre-heat temperature is 50-500°C, preferably 150 to 450°C.

The feed may be fed into the reaction chamber at a rate of
10 suitably from 10 to 10,000, preferably from 500 to 8000 gas hourly space velocity. It will of course be understood that the GHSV will vary for different feed compositions. The gas hourly space velocity may be defined for the purposes of the present invention as

$$15 \quad \text{GHSV} = \frac{\text{volume of total feed at STP}}{\text{Time} \times \text{volume of catalyst bed}}$$

The process may be carried out in any suitable reactor, for example a fixed bed, a fluidised bed, a slurry reactor or a continuous catalyst regeneration reactor.

20 The process of the present invention provides a good conversion of ethene. Conversion can exceed 40% of ethene, preferably at least 50%.

The products of the process of the present invention suitably contain branched olefinic hydrocarbons, especially iso-
25 butene and iso-pentenenes. Typically, the selectivity to these branched olefins is greater than 30%, especially greater than 40%. Additional products may include gaseous linear butenes and pentenes and a liquid product consisting essentially of C₆ and C₇ olefins with a lesser amount of C₈ to C₁₀ olefins and traces of
30 C₁₁ to C₁₂ olefins. A small amount of by-products such as C₁ to C₁₀ alkanes and aromatic hydrocarbons may also be obtained.

If desired, unreacted feed olefins may be separated from the product stream and recycled back into the reaction chamber. Liquid olefins such as C₆ to C₁₀ olefins may also be separated
35 from the product stream and recycled to the reaction chamber

either in addition to or substantially as the sole source of the C₃ to C₁₀ olefin feed.

Where the feed stream contains substantial amounts of light alkanes, e.g. C₁ to C₃ alkanes or other diluents such as may be
5 found in a catalytic cracker fuel gas stream, it is preferable not to recover unreacted ethylene.

A portion of the liquid products may be suitably removed by use of a continual bleed stream to avoid the build up of unreactive aromatic and paraffinic hydrocarbons. The desired
10 products, namely the isobutenes and the isopentenes, may be isolated from the linear isomers through distillation or selective absorption.

Recovery of the branched isomers may also be effected through the further conversion to other desirable products, either
15 as individual C₄ and C₅ streams or as a mixed C₄ and C₅ stream. A typical process is the etherification of the branched C₄ and C₅ isomers within the normal/iso olefin mixture with an alcohol to yield valuable branched ethers. Suitable alcohols include alkanols having 1 to 8 carbon atoms, for example, methanol,
20 ethanol, 1-propanol, iso-propanol, 1-butanol and 2-butanol. Suitably, the branched olefin and the alcohol are reacted in equimolar quantities or either reactant may be in molar excess. Preferably, equimolar quantities of the alcohol and branched olefin are reacted. The reaction with methanol to yield methyl
25 tertiarybutyl ether (MTBE) and tertiaryamyl methyl ether (TAME) is particularly preferred.

A further conversion process suitable for the recovery of the branched olefins is the polymerisation to polyisobutene (PIB), copolymerisation of isobutene and isopentene, and/or
30 polyisopentene (PIP). This polymerisation reaction may suitably be carried out in the liquid phase at sub-ambient temperatures. Suitable catalysts for the polymerisation reaction include alkylaluminium halides promoted by alkyl halides or boron trifluoride.

35 A still further conversion process is suitably the acid

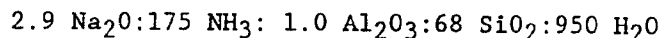
catalysed hydration to yield isobutanol and/or isopentanol.

The residual linear olefins may suitably be recycled to the reaction chamber either in addition to or as substantially the sole source of the C₃ to C₁₀ olefinic co-feed. Alternatively, the linear isomers may be structurally isomerised to yield a mixture of branched and linear isomers before being passed to the separation unit. Details of this process are disclosed in European Patent No. 0247802. Suitably, a portion of the linear C₄ and C₅ isomers may be removed by a continuous bleed stream to avoid build up of unreactive butanes and pentanes. Furthermore, alkylation of the linear olefins will suitably produce aliphatic hydrocarbons suitable for gasoline blending or if so desired, aromatisation of the linear olefins may suitably provide aromatic hydrocarbons suitable for gasoline blending.

The invention will now be described in detail with reference to the following Examples:

Example 1: Synthesis of Theta-1 Zeolite

Theta-1 was synthesised using ammonia as the templating agent. Sodium aluminate (30 g, ex BDH, 40 wt% Al₂O₃, 30 wt% Na₂O and 30 wt% H₂O) and sodium hydroxide (15.6 g ex BDH) were dissolved in distilled water (240 g). Ammonia solution (1400 g, SG 0.90° containing 25% NH₃) was added with gentle mixing. Silica gel sold under the trademark Ludox AS40 (1200 g) which contained 40 wt% silica was added over fifteen minutes with stirring to maintain a homogeneous hydrogel. The molar composition of the hydrogel was:



The mixture was then loaded into a 5 litre Parr autoclave and crystallised at 175°C for 25 hours under autogeneous pressure whilst mixing by a mechanical stirring action. At the end of the crystallisation period the autoclave was cooled, and the product filtered, washed and dried in an air oven at 100°C. The crystallinity and the purity of the zeolite were determined by X-ray powder diffraction. The sample contained Theta-1 zeolite with estimated amount of cristobalite of less than 5%. The Theta-1 as

synthesised which contained both Na^+ and NH_4^+ ions was directly ion exchanged in order to remove the Na^+ ions. The zeolite was mixed for one hour with an aqueous ammonium nitrate solution (1M, zeolite to solution weight ratio of 1:20). The zeolite was
5 filtered, washed and the ion exchange treatment repeated twice. The ammonium form of the zeolite was then dried at 100°C and calcined overnight in air at 550°C to convert it to the hydrogen form. The X-ray diffraction pattern of the H-form is shown in Table 1.

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TABLE 1: XRD OF PRODUCT OF EXAMPLE 1

2 THETA	D SPACINGS	RELATIVE INTENSITIES
	A°	100 x I/I _{max}
8.17	10.81	100
10.16	8.70	22
12.81	6.91	23
16.36	5.42	11
19.42	4.57	12
20.36	4.36	97
24.22	3.67	82
24.64	3.61	52
25.76	3.46	36

Variation in intensities of $\pm 20\%$.

Variation in 2 theta positions of $\pm 0.2^\circ$ with corresponding variation in D spacings.

Peaks below 10% of I_{max} excluded

Copper alpha-1 wavelengths, 1.54060

X-ray Diffractometer Philips PW 1820/00

Slits $1/4^\circ$, 0.2° , $1/4^\circ$

2 Theta Scan $2^\circ - 32^\circ$

Step Scan 0.025°

Time 4 sec

Example 2: Catalyst Steaming and Acid Treatment of H-Theta-1

The H-form of the zeolite as prepared in Example 1 was pressed under 10 tonnes pressure into tablets which were broken into granules and these in turn were sieved to pass 600 micron, but not 250 micron sieves. The granules were placed in a tubular reactor (60 mm ID) and heated to 550°C. There was a large pre-heating zone in which water was converted to steam before it came into contact with the catalyst granules. Distilled water and nitrogen were passed through the preheating zone over the catalyst at a range of 30 grams/hour and 60 ml/minute respectively. After two hours with the reactor temperature at 550°C, the water flow was stopped and the catalyst was cooled to ambient temperature. The steam catalyst was then reacted in refluxing 1M aqueous nitric acid for one hour, filtered and then washed with distilled water. This acid treatment procedure was repeated twice. The zeolite powder was then dried and then calcined at 550°C in air for 12 hours.

Example 3: Preparation of H-Ga-TON

Gallosilicate TON was prepared as detailed in example 1 of EP-A-0106478. It was converted to the hydrogen form (H-GaTON) as follows. The as synthesised material was calcined at 550°C for 6 hours to remove the template. Residual sodium ions were exchanged for NH_4^+ by stirring with aqueous ammonium nitrate solution for a minimum of two hours (1M, gallosilicate to solution weight ratio 1:20). The gallosilicate was filtered, washed with distilled water, and the ion exchange treatment repeated twice. The ammonium form of the gallosilicate was then dried at 100°C and calcined at 550°C in air for 6 hours to convert it to the hydrogen form.

Example 4: Preparation of H-ZSM-23

ZSM-23 was synthesised using diisopropanolamine as the templating agent according to GB patent application No. 2190910. This material was converted to the hydrogen form (H-ZSM-23) as follows. The as synthesised material was calcined at 550°C for 6 hours to remove the template. Residual sodium ions were exchanged

for NH_4^+ by stirring with aqueous ammonium nitrate solution at 80°C for three hours (1.5M, ZSM-23 to solution weight ratio 1:10). The product was filtered, washed with distilled water, and the ion exchange treatment repeated twice. The ammonium form of the zeolite was dried at 100°C and calcined at 550°C in air for 6 hours to convert it to the hydrogen form.

Example 5: Preparation of H-FER

Ferrierite was synthesised using a 1-methylpiperidine template as follows. Sodium aluminate (40 wt% Al_2O_3 , 24.3 wt% Na_2O , 28.3% H_2O and 7.4% NaOH) 3.83g was dissolved in water (61.5g), and to this was added potassium hydroxide (2.18g) and 1-methylpiperidine (2.98g) with vigorous stirring. After 5 minutes 33.74g of silica gel containing 40 wt% silica (sold under the Trademark Ludox AS40) were slowly added to form a thick hydrogel. The resulting hydrogel was stirred for 30 minutes. A portion of this gel was loaded into a rotating stainless steel autoclave, which was maintained at 180°C for 4 days to induce crystallisation. The ferrierite product was recovered by filtration, washed with distilled water and dried at 100°C .

This material was converted to the hydrogen form (H-FER) as follows. The as synthesised ferrierite was calcined in nitrogen at 450°C for 16 hours to remove the 1-methylpiperidine template. Sodium and potassium ions were exchanged for ammonium ions by refluxing in aqueous ammonium nitrate solution (1M, ferrierite to solution weight ratio 1:10). The product was collected by filtration, washed, and the procedure repeated twice before drying at 100°C . The ammonium form was converted to the hydrogen form (H-FER) by calcination in air at 550°C for 16 hours prior to testing.

Example 6: Preparation of H-EU-1

Zeolite EU-1 was synthesised using a dual tetramethylammonium/hexamethonium bromide ($[(\text{CH}_3)_3\text{N}(\text{CH}_2)_6\text{N}(\text{CH}_3)_3]2\text{Br}\cdot\text{H}_2\text{O}$) template. Sodium aluminate (0.38g, 40wt% Al_2O_3 , 30wt% Na_2O , 30wt% H_2O) and KOH (1.0g) were dissolved in water (20 ml). Ludox (40% SiO_2) was added to give a gel, which

was stirred for one hour. Tetramethyammonium hydroxide (6.48g) and hexamethonium bromide (6.48g) in water (38.7 ml) were added to the gel, which was stirred for a further hour. The gel was loaded into a stainless steel rotating autoclave, and was crystallised at 180°C for 173 hours under autogeneous pressure. After recovery by filtration, the crystalline EU-1 product was washed with water and dried at 100°C. The as synthesised material was calcined at 550°C for 6 hours to remove the template. Potassium and sodium ions were exchanged for NH_4^+ by stirring at room temperature with aqueous ammonium nitrate solution for a minimum of two hours (1M, zeolite to solution weight ratio 1:10). The zeolite was filtered, washed with distilled water, and the ion exchange treatment repeated twice. The ammonium form of the zeolite was then dried at 100°C and calcined at 550°C in air for 6 hours to convert it to the hydrogen form.

Example 7: Preparation of H-SAPO-11

SAPO-11 was prepared using a diisopropylamine templating agent. Aluminium isopropoxide (41 g) was added to 40 ml of water with overhead stirring. After 20 minutes, a solution of 85% phosphoric acid (22.25 g) in water (5 ml) was added to give a thick gel. To this was added diisopropylamine (20.3 g), nickel nitrate nonahydrate (0.22 g), LUDOX (40% SiO_2 , 4.5 g) and water (52.6 g). The resultant thick gel was placed in a sonic bath for three minutes, and then triturated in a pestle and mortar to give a smooth gel. This was loaded into a teflon lined rotating autoclave, and crystallised under autogeneous pressure at 175°C for 50 hours. After cooling, the SAPO-11 product was recovered by centrifugation and washed with water before drying at 100°C.

Example 8

The H-form of Theta-1, prepared as described in Examples 1 and 2, was pressed into tablets at 10 tonnes pressure. The tablets were then broken and sieved into granules to pass 600 micron, but not 250 micron sieves. A charge of 10 ml of catalyst granules was loaded into a tubular reactor with a coaxial thermocouple well. The reactor was heated to 420°C and

ethene/propene feeds were fed into the reactor at a flow rate of approximately 240 ml/min. Conversion and selectivities were evaluated after 30 minutes on stream.

The terms used in Table 2 and the following Tables are defined as follows:

Conversion	Carbon molar conversion
Selectivity	<u>Carbon molar yield of each component x 100%</u> total carbon molar conversion
C_2H_4	ethene
10 C_3H_6	propene
i- C_4	iso-butene
n- C_4	n-butenes
i- C_5	iso-pentenenes
n- C_5	n-pentenenes
15 C_6+	C_6 - C_{17} alkanes/alkenes, predominantly C_6 to C_{10} olefins
Aromatics	Benzene, C_1 to C_4 benzenes

Example 9

The general process of Example 8 was repeated for a mixed feed of 2:1 (66.6/33.3%) ethene to propene using the various catalysts prepared according to Examples 3 to 7. The mixed feed was fed into the reactor under a gas hourly space velocity of 1440 h^{-1} and the reaction was carried out at 420°C . Conversion and selectivity values were determined after 30 minutes on stream. The results are given in Table 3.

Comparative Example 1

The procedure of Example 8 was repeated but passing a feedstock of ethene over H-Theta-1. The results are shown in Table 4. A pure ethene feed gives reasonably high selectivity to C_4/C_5 product but at low conversion.

Comparative Example 2

The procedure of Example 8 was repeated but passing a feedstock of propene over H-Theta-1. The results are given in Table 4. A pure propene feed provides a high yield of C_6+ products, principally hexenes.

Comparative Example 3

The process of Example 9 was repeated using H-ZSM-5 as the catalyst. The ammonium form of ZSM-5 was purchased from PQ Corporation (VALFOR CBV 3002) and converted to the hydrogen form by calcination in air at 550°C for 16 hours prior to testing. The results are given in Table 4. It can be seen that whilst high conversion of ethene is possible, low selectivities to iso-butenes and iso-pentenenes are achieved.

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TABLE 2

Catalyst	Feed (%)		Conversion (%)		Selectivity (% C mol)						
	C ₂ H ₄	C ₃ H ₆	C ₂ H ₄	C ₃ H ₆	i-C ₄	n-C ₄	i-C ₅	n-C ₅	C ₁ -C ₄ alkanes	C ₆ +	Aromatics
H-Theta 1	66.6	33.3	59.1	65.2	10.8	14.0	28.2	14.3	6.0	26.4	0.4
H-Theta 1	80	20	44.6	63.5	10.6	14.1	33.2	14.5	6.2	20.9	0.4

TABLE 3

Catalyst	Conversion (%)		Selectivity (% C mol)						
	C ₂ H ₄	C ₃ H ₆	i-C ₄	n-C ₄	i-C ₅	n-C ₅	C ₇ -C ₄ alk	C ₆ +	Arom
Ga-TON	28.2	57.2	12.7	16.1	28.1	8.4	3.4	29.0	2.4
ZSM-23	67.5	73.1	9.7	12.0	19.6	7.4	12.3	34.6	4.4
FER	19.1	49.2	5.1	7.0	45.9	13.9	1.8	25.8	0.5
EU-1	13.1	52.8	16.5	19.2	22.3	6.6	5.3	28.7	1.4
SAPO-11	17.6	55.7	5.8	7.5	33.6	12.5	2.1	37.4	1.0

TABLE 4

Catalyst	Feed (%)		Conversion (%)		Selectivity (% C mol)							
	C ₂ H ₄	C ₃ H ₆	C ₂ H ₄	C ₃ H ₆	i-C ₄	n-C ₄	i-C ₅	n-C ₅	C ₁ -C ₄ alk	C ₆ +	Arom	
H-Theta-1	100	0	23.9	-	12.6	16.9	27.9	11.9	2.9	11.7	0	
H-Theta-1	0	100	-	81.6	8.9	10.5	11.0	4.5	6.2	54.6	1.4	
H-ZSM-5	66.6	33.3	97.7	89.5	1.9	2.3	1.8	3.4	38.4	14.2	38.1	

Claims:

1. A process for the production of a product containing at least one C₄ and C₅ branched olefin which comprises passing a feedstock containing ethene over a zeo-type catalyst in a reaction chamber characterised in that the feedstock also comprises at least one C₃ to C₁₀ olefin, and being present in the ethene feedstock at a concentration of up to 50% v/v relative to ethene and the zeo-type catalyst having a framework structure which includes a 10-member channel that is not intersected by another 10- or 12- member channel.
2. A process according to claim 1 in which the feedstock comprises from 10 to 35% v/v C₃ to C₁₀ olefin.
3. A process according to claim 1 or claim 2 in which the C₃ to C₁₀-olefin is propene.
4. A process according to any one of the preceding claims in which the zeo-type catalyst is selected from the following structural types: TON, MTT, EUO, AEL and FER.
5. A process according to claim 4 in which the zeo-type catalyst has TON- or FER- type structure.
6. A process according to any one of the preceding claims in which the reaction temperature is from 200 to 700°C and the pressure is from 0.1 to 100 bar absolute.
7. A process according to any one of the preceding claims in which the gas hourly space velocity of the feed is from 10 to 10,000 hr⁻¹.
8. A process according to any one of the preceding claims in which

the feedstock is derived from refinery processes; catalytic cracking processes; stream cracking of naphtha and higher hydrocarbons; conversion of alcohols; or the partial oxidation of hydrocarbons.

5 9. A process according to any one of the preceding claims in which the C₄ and/or C₅ branched olefinic products are further reacted with an alcohol to produce at least one ether.

10. A process according to claim 9 in which the alcohol is methanol.

10 11. A process according to any one of claims 1 to 8 in which the C₄ and/or C₅ branched olefinic products are converted to polyisobutene, polyisopentene and/or a copolymer of polyisobutene and polyisopentene.

12. A process according to any one of claims 1 to 8 in which any
15 C₆ to C₁₀ product olefins are recycled back to the reaction chamber.

13. A process according to any one of claims 9 to 12 in which any unreacted linear olefins are recycled back to the reaction chamber.

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 93/02407

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C07C2/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,4 227 992 (GARWOOD ET AL) 14 October 1980 cited in the application see claims ---	1-3
X	EP,A,0 034 444 (MOBIL OIL CORPORATION) 26 August 1981 see claims ---	1,4
X	EP,A,0 269 503 (INSTITUT FRANCAIS DU PETROLE) 1 June 1988 see claims ---	1,4,5
X	EP,A,0 311 310 (MOBIL OIL CORPORATION) 12 April 1989 see claims -----	1,4,5

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
 "E" earlier document but published on or after the international filing date
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 "O" document referring to an oral disclosure, use, exhibition or other means
 "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
 "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
 "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
 "&" document member of the same patent family

Date of the actual completion of the international search

14 February 1994

Date of mailing of the international search report

25.02.94

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
 Fax: (+31-70) 340-3016

Authorized officer

Van Geyt, J

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 93/02407

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